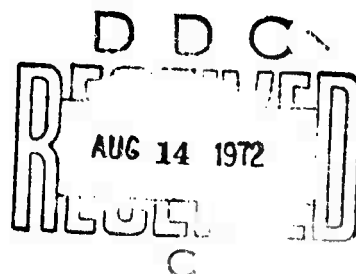RADC-TR-72-161
Technical Report
May 1972

METAL OXIDE STUDIES

General Electric Company
Space Science Lab.

Sponsored by
Defense Advanced Research Projects Agency
ARPA Order No. 1649

D D C
AUG 14 1972
C

Approved for public release;
distribution unlimited.

The views and conclusions contained in this document are those
of the authors and should not be interpreted as necessarily
representing the official policies, either expressed or implied,
of the Defense Advanced Research Projects Agency or the U. S.
Government.

Rome Air Development Center
Air Force Systems Command
Griffiss Air Force Base, New York

When US Government drawings, specifications, or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded, by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

ACCESSION for

FTIS   White Section   ☑
F C   Buff Section   ☐
UNA . OUNCED
JUSTIFICATION ....   ☐

....

BY ....
DISTRIBUTION/AVAILABILITY CODES

Dist.   AVAIL. and/or SPECIAL

A

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
General Electric Company Space Sciences Laboratory King of Prussia, Penna. 19406	Unclassified
	2b. GROUP

3. REPORT TITLE

Metal Oxide Studies

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final

5. AUTHOR(S) (First name, middle initial, last name)

Dr. Milton J. Linevsky

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May, 1972		17

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
F30602-69-C-0380	
b. PROJECT NO. ARPA Order 1649	
c. Program Code 0E20	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	RADC-TR-72-161

10. DISTRIBUTION STATEMENT

Approved for public release;
distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
Monitored by: Joseph J. Simons RADC (OCSE), GAFB, NY 13440	Advanced Research Projects Agency 1400 Wilson Blvd. Arlington, Va. 22209

13. ABSTRACT

Emission and absorption spectra over mixtures of liquid uranium-urania have been obtained using the carbon-tube furnace facility. In the temperature range of approximately $2100^{\circ}C$ to $2400^{\circ}C$ a complex system of bands has been observed in the region of 4800A to 7000A. The wavelength region from 5900A to 6000A is especially noteworthy since it contains a very intense highly dense band system. By comparison with the temperature coefficient of a known uranium line it was shown that the most intense feature in this region was due to either UO or UO_2. No complete analysis has been carried out, however, preliminary indications from the complexity of the spectra points to UO_2 as the most likely species giving rise to the observed spectra.

Flame studies have been initiated using UF_6 seeded into cyanogen/oxygen and hydrogen/nitrous oxide flames. Spectra of these flames have been observed and are completely different in nature from the furnace results. The flame spectra appear to be continuous with no line structure evident. The predominant uranium species in these flames should be the higher oxides, e.g. UO_3, rather than U, UO, or UO_2. Further work is continuing.

The oscillator strength of the (0,0) and the (1,1) band of the $E^1\Sigma \to X^1\Sigma$ transition in ThO has been obtained. The spectra were observed in absorption over mixtures of liquid thorium-thoria and total absorption measurements of several rotational lines in the band were carried out. From a knowledge of the vapor pressure of ThO at various temperatures a curve growth was constructed and the oscillator strength obtained. $f_{0,0}$ was found to be approximately 0.08. From the relative intensity of the (1,1) band head to the (0,0) head, $f_{1,1}$ was found to be approximately 0.06. Further work is continuing on other bands for ThO.

DD FORM 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

1a

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Uranium oxides						
Thorium oxide						
Spectra						
Oscillator strengths						

i b

METAL OXIDE STUDIES

Dr. Milton J. Linevsky

Contractor: General Electric Co., Space Science Lab
Contract Number: F30602-69-C-0380
Effective Date of Contract: 1 July 1969
Contract Expiration Date: 31 December 1972
Amount of Contract: $264,725.00
Program Code Number: 2E20

Principal Investigator: Dr. Milton J. Linovsky
                Phone: 215 962-3495

Project Engineer: Joseph J, Simons
                Phone: 315 330-3451

Approved for public release;
distribution unlimited.

1C

FOREWORD

This study is being performed at General Electric Company, Space Sciences Laboratory, King of Prussia, Pa., 19406, for the Advanced Research Projects Agency, Washington, D. C., Rome Air Development Center Griffiss Air Force Base, New York, is monitoring the study for ARPA, under Contract F30602-69-C-0380, Project 1649. Mr. Joseph J. Simons (OCSE) is the RADC Project Engineer.

Distribution of this report is limited by the Mutual Security Act of 1949.

This technical report has been reviewed and is approved.

PUBLICATION REVIEW

This technical report has been reviewed and is approved.

RADC Project Engineer

SUMMARY

Emission and absorption spectra over mixtures of liquid uranium-urania have been obtained using the carbon-tube furnace facility. In the temperature range of approximately $2100^{\circ}C$ to $2400^{\circ}C$ a complex system of bands has been observed in the region of 4800 A to 7000 A. The wavelength region from 5900 A to 6000 A is especially noteworthy since it contains a very intense highly dense band system. By comparison with the temperature coefficient of a known uranium line it was shown that the most intense feature in this region was due to either UO or UO_2. No complete analysis has been carried out, however, preliminary indications from the complexity of the spectra points to UO_2 as the most likely species giving rise to the observed spectra.

Flame studies have been initiated using UF_6 seeded into cyanogen/oxygen and hydrogen/nitrous oxide flames. Spectra of these flames have been observed and are completely different in nature from the furnace results. The flame spectra appear to be continuous with no line structure evident. The predominant uranium species in these flames should be the higher oxides, e.g. UO_3, rather than U, UO, or UO_2. Further work is continuing.

The oscillator strength of the (0, 0) and the (1, 1) band of the $E\,^1\Sigma \rightarrow X\,^1\Sigma$ transition in ThO has been obtained. The spectra were observed in absorption over mixtures of liquid thorium-thoria and total absorption measurements of several rotational lines in the band were carried out. From a knowledge of the vapor pressure of ThO at various temperatures, a curve of growth was constructed and the oscillator strength obtained. $f_{0,0}$ was found to be approximately 0.08. From the relative intensity of the (1, 1) band head to the (0, 0) head, $f_{1,1}$ was found to be approximately 0.06. Further work is continuing on other bands for ThO.

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

I.   INTRODUCTION

This report describes a continuation of an experimental study aimed at obtaining information relevant to several ARPA programs. Of particular concern is the evaluation of the importance of certain metal oxides to Project Ivy Owl.

The objectives of the past six months efforts were: 1) to perform spectroscopic studies on the uranium/uranium oxide system in an attempt to obtain in a controlled manner the absorption spectrum of UO and to further the understanding of U/O spectroscopy and 2) attempt to obtain oscillation strength information on various transitions in the electronic spectrum of ThO.

Attempts to obtain characteristic band spectra of UO have been for the most part unsuccessful (Ref. 1 - 3). Indeed only the results of Gatterer (Ref. 1) on arc discharges between uranium electrodes have indicated any discrete - like spectra due to uranium containing species. The studies in seeded flames (Ref. 2) and by laser vaporization "blow-off" (Ref. 3) have yielded at best what appears to be continuum like spectra in the visible and near u.v.   Based on existing thermodynamic information for the species UO, UO_2, and UO_3' (see Ackermann et al Ref. 4 and DeMaria et al Ref. 5), it can be shown that in the temperature range of several thousand degrees, at equilibrium, under conditions similar to those encountered in flames and possibly in blow-off experiments, the predominant vapor species is the highest oxide, i.e. UO_3. Therefore, it is not surprising to find that flames and laser blow-off plumes have yielded little information concerning the spectroscopy of UO or UO_2. In order to favor the existence of these lower oxides a more reducing environment must be established. In the study reported by Ackermann et al (Ref. 4), the predominant molecular vapor species over mixtures of uranium and uranium oxide was found to be UO and UO_2. Similarly these species were observed in the mass spectrometric investigation by DeMaria et al (Ref. 5), on the vaporization from mixtures of uranium and aluminum oxide. In the former study, for example, at $2000^{\circ}K$ the partial pressures of UO and UO_2 in equilibrium with urania - liquid

1

uranium was found to be approximately 5×10^{-6} atm. and 6×10^{-7} atm. respectively. It is interesting to note that the corresponding partial pressure of O-atoms was found to be less than 10^{-13} atm. Clearly in order to produce spectroscopically significant qualities of UO and/or UO_2 oxygen must be excluded from the system.

In the present study the carbon - tube furnace facility was used to generate molecular uranium oxide species under conditions very similar to those reported above. In this fashion spectra both in absorption and emission have been obtained which are line-like in nature and most likely due to UO or UO_2. No complete analysis has yet been carried out. Preliminary indications point to UO_2 as the principle species observed.

Seeded flame studies have also been initiated in order to investigate the radiative properties of higher oxide species. These studies have just gotten under-way and the results are preliminary. The nature of the emission thus far observed is completely different from that seen in the furnace.

In the case of ThO, the spectroscopy of this molecule appears to be fairly well understood and many transitions have been assigned (see a recent review by Wentink and Spindler Ref. 6). However, no absolute intensity data have been reported on any of these transitions. Again the carbon - tube furnace was used to generate a known concentration of ThO in the gas phase and subsequent absorption measurements on the $E {}^1\Sigma \rightarrow X {}^1\Sigma$ transition allowed the determination of the oscillation strengths for the $(0, 0)$ and $(1, 1)$ bands.

II. URANIUM OXIDES

1. Furnace Studies

The carbon tube furnace facility has been described in detail elsewhere (Ref. 7). Approximately equal amounts of powdered uranium metal and uranium dioxide (obtained from the K and K Laboratories) were thoroughly mixed and loaded into a tantalum boat contained in a tantalum-lined cylindrical carbon cell. The inside length of the cell was approximately $4\frac{1}{2}$ inches. Tantalum lined carbon end pieces with $\frac{1}{4}$ inch openings were fitted into the ends of the cell and served to allow light to pass through the cell. The cell was placed in the center of the carbon tube furnace and thoroughly degassed under vacuum at approximately 1500°C. After several hours of degassing, helium gas (O_2 impurities removed by passing over red-hot titanum metal) was admitted to the furnace to a pressure of 1 atm. The furnace temperature was gradually raised and spectral observations were made both in apsorption and emission using the 2 meter Bausch and Lomb dual grating spectrograph.

At approximately 2000°C the onset of a complex system of bands was observed. Under relatively low resolution these bands appeared to be diffused in nature and extended from approximately 4800 $\overset{o}{A}$ to 7000 $\overset{o}{A}$. A very intense line like feature at 5935 $\overset{o}{A}$ is especially evident. In addition, a great many uranium I lines are seen and have been identified by comparison with reported spectra (Ref. 8 and 9). The nominal plate dispersion was approximately 8A/mm. Similarly, spectra have also been observed at higher resolution in the 2nd order of the 30,000 line/inch grating. The nominal plate dispersion was approximately 2A/mm. In this case those features especially in the 5900 $\overset{o}{A}$ to 6000 $\overset{o}{A}$ region which previously appeared diffuse in nature now are seen to be line-like with many close lying lines throughout. In Figure 1 is shown a typical absorption spectrum at relatively low resolution in the spectral region of approximately 5000 $\overset{o}{A}$ to 6900 $\overset{o}{A}$. This spectrum was obtained using a high pressure Xenon arc as a source and the cell temperature was approximately 2300°C. (The uranium oxide spectrum is the upper dark lined spectra while the lower white lined
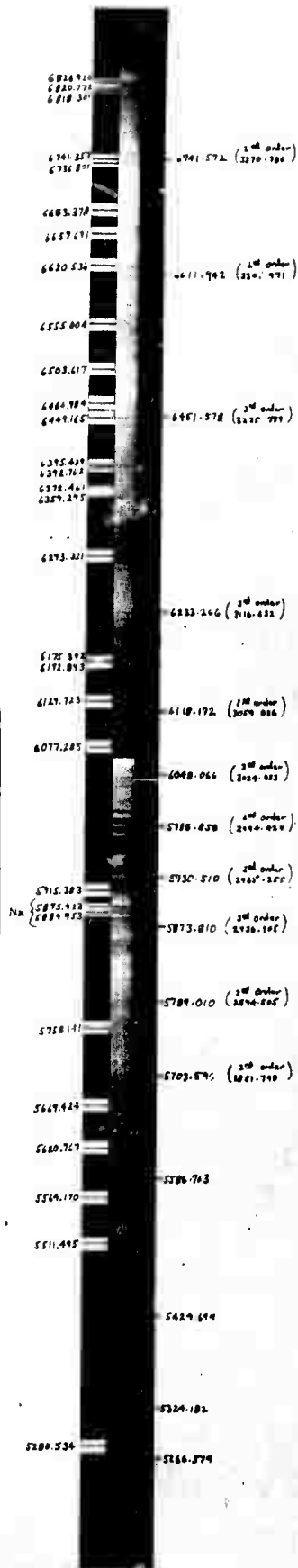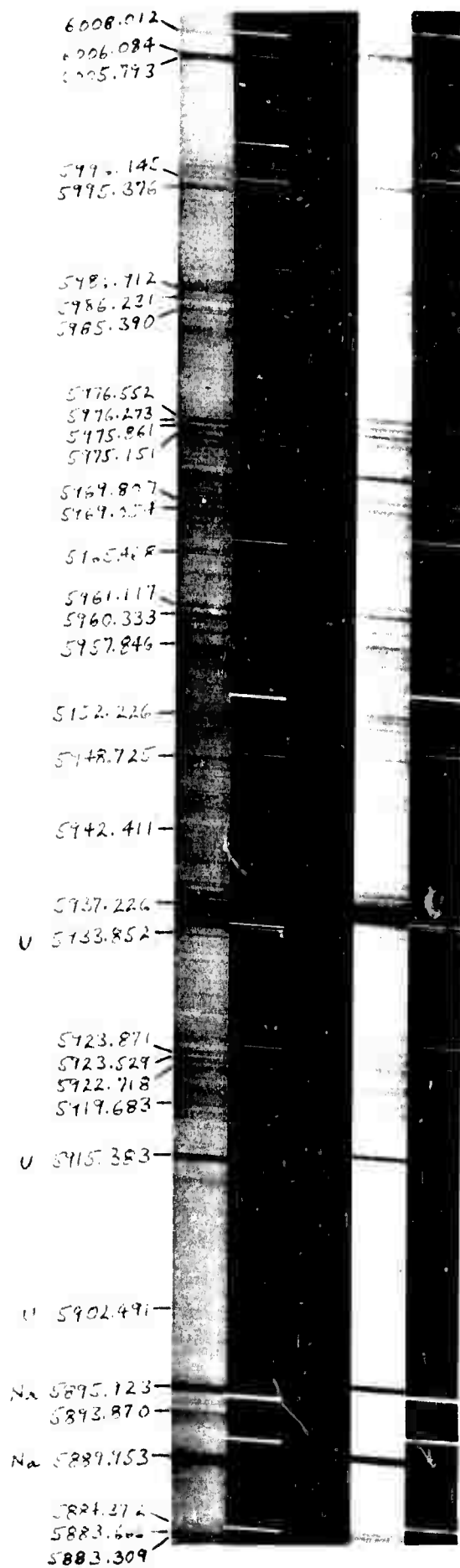
3

Figure 1. Uranium Oxide Spectra – Low Resolution

Figure 2. Uranium Oxide Spectra – Moderate Resolution

5

spectrum is an iron comparison. The abrupt change in shading at approximately 6067Å is not real. Uranium I lines have been identified). The corresponding absorption spectrum obtained at higher resolution in the 5900Å to 6000Å region is shown in Figure 2. Wavelength identification of significant uranium oxide features is included in this spectrum. The densely packed line structure should be noted.

These spectra were also observed photometrically using a Spex 1500 monochromator both in absorption and emission. An EMI 9558, S-20 photomultiplier and P.A.R. lock-in amplifier and chopper were used to monitor and record the spectrum. In order to help determine the nature of the carrier of the strong feature at 5935 A, the temperature dependence of the absorption centered at 5935 A relative to the strong uranium I line at 5915 A was carried out. Ackermann et al (Ref. 4) have given the following observed heats of vaporization of U, UO and UO_2 from mixtures of urania-liquid uranium: 116, 123, and 138 k cal/mole respectively. The uranium I line at 5915 A involves the ground state and, if the feature at 5935 A also involves the ground states of either UO or UO_2, then from the above heats of vaporization it is expected that the two features will have the same temperature dependency within approximately 20%. This is fully borne out by the results of the photometric measurements made on these features. A log-log plot of the quantity $T \log {}^I o/I$ for 5915 A (UI) against that for the unknown features at 5935 A ($T \log {}^I o/I$ is proportional to the vapor pressure) yields a straight line whose slope is $1 \pm .2$. This is shown in Figure 3. Therefore, it must be concluded that the strong feature at 5935Å is due to the uranium oxide UO or UO_2. It is not possible from the temperature dependency to decide which oxide gives rise to the observed spectra.

Attempts to carry out a vibrational analysis of the spectra shown in Figures 1 and 2 have met with very limited success. Abramowitz (Ref. 10) using matrix isolation techniques, has reported the vibrational spacing for supposedly ground state $U^{16}O$ to be 776 cm^{-1}. A matrix shift of approximately 10% to 15% for this molecule would not be unreasonable. Therefore, a vibrational spacing of approximately 800 $\pm$ 100 cm^{-1} would be expected to be reflected in the spectra given in

Figure 3. Absorption Intensity 5915 A UI vs 5935 A Feature

SLOPE = 1 ± .2

$T \, LOG \left(\frac{I_o}{I} \right)$ 5935 A
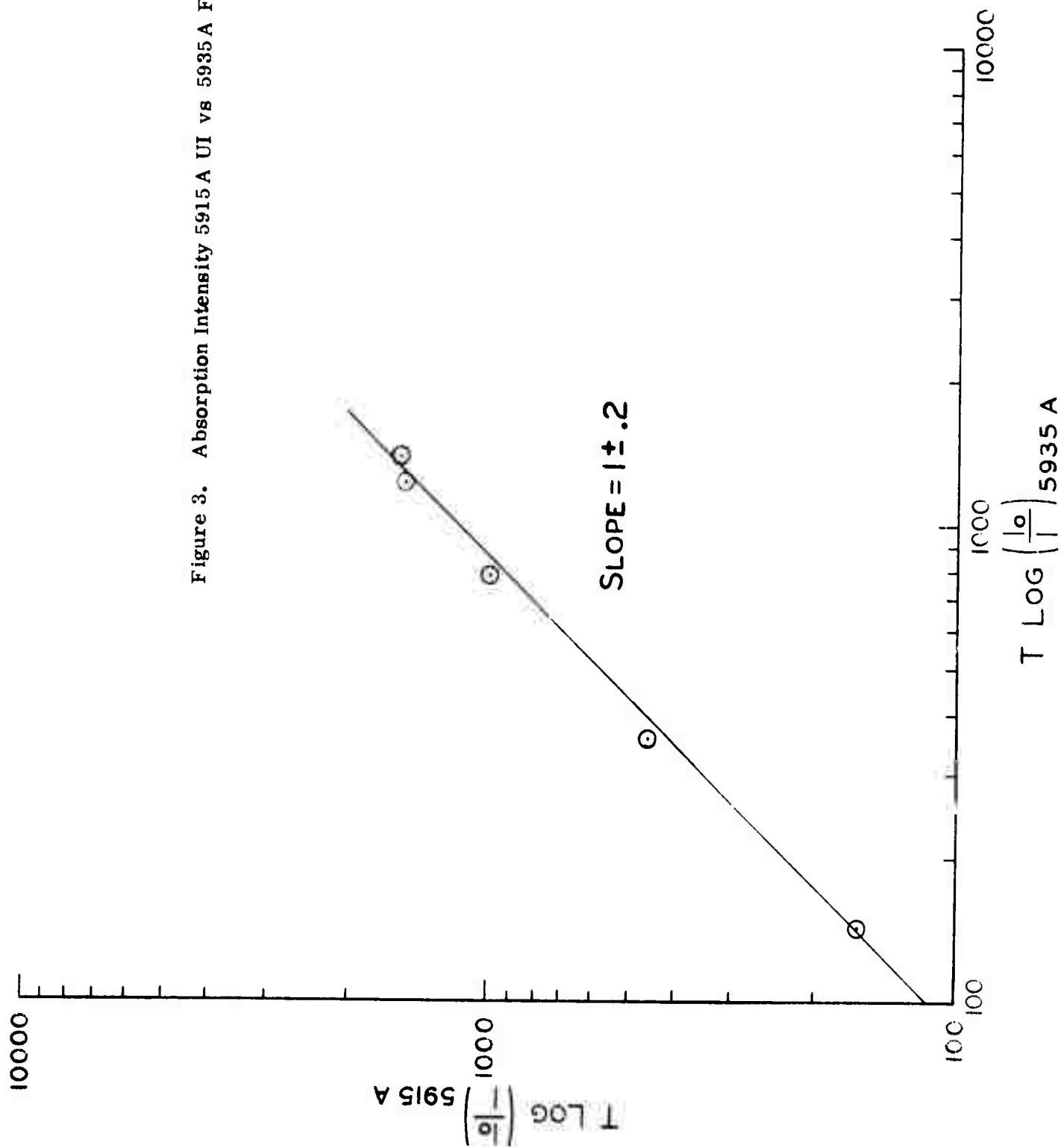
$T \, LOG \left(\frac{I_o}{I} \right)$ 5915 A

7

Figure 1 and 2. No progression with this spacing is observed. On the other hand, if UO_2 is the carrier of the observed spectra, progressions in both the symmetric stretching mode, ν_1, and the bending mode ν_2 should be evident. Abramowitz (Ref. 10) has also reported a value of approximately 81 cm^{-1} for ν_2 and a value of 874 cm^{-1} for one of the stretching modes in $U^{16}O_2$. These frequencies again being observed in argon matrices. From an examination of the spectra reported here especially that given in Figure 2, it is possible to pick out a progression of bands that could possibly correspond to the bending mode spacing (i.e. 60 cm^{-1} to 90 cm^{-1}). Another progression in this spectrum appears to have a spacing around 400 cm^{-1}. This could conceivably correspond to the spacing due to a progression in ν_1. At the present time it has not been possible to carry out a complete vibrational analysis. However, it is felt that UO_2 is most likely responsible for the observed spectra.

2. Flame Studies

A preliminary investigation of uranium oxide spectra in high temperature flames has been initiated. Uranium hexafluoride has been seeded in small quantities into cyanogen-oxygen and nitrous oxide-hydrogen flames burned at atmospheric pressure. The addition of UF_6 has been found to give rise to relatively strong continuous radiation in the wavelength region from about 2000 Å to at least 8000 Å. Extension of these measurements to the infrared region are currently planned.

Nitrous oxide - hydrogen and cyanogan - oxygen flames were supported on a water cooled Meker type burner. Gases were individually metered and premixed before entering the burner chamber. Small quantities of UF_6, approximately 5% in argon, were introduced into the unburned gases, spectra were taken of both the seeded and unseeded flames and the contribution to radiation by uranium species obtained by difference. Spectroscopic measurements in the flame were made in a volume element approximately 3 cm above the burner top (reaction zone) where the flame gases are in thermodynamic equilibrium. Spectra were obtained using an EG&G 580 series spectral radiometer equipped with both UV and visible gratings, and also with

a Bausch and Lomb 2 meter grating spectrograph.

Figure 4 shows typical wavelength distributions of the uranium species emission in a cyanogen oxygen flame having a calculated adiabatic flame temperature of about $3900^{\circ}K$. The continuum emission from somewhat cooler burning UF_6 seeded nitrous oxide/hydrogen flames (T $\approx$ $2900^{\circ}K$) was similar to that in the cyanogen oxygen flames. In both types of flames the continuum is observed to have intensity maximum at about 3500 and $5900\overset{o}{A}$ and an apparent short wavelength cut off at about $2200\overset{o}{A}$.

In separate experiments, equivalent or greater flows of COF_2 were substituted for the UF_6/Ar mixtures seeded into the cyanogen oxygen flames. Absence of enhanced continuum emission in these experiments indicated that fluorine atom radiative recombination was not responsible for the continuum observed upon UF_6 addition. Uranium seeding into the cyanogen oxygen flame by entrainment of sprayed droplets of aqueous uranyl nitrate solution into unburned gas flows resulted in a spectrum similar to that observed with UF_6 but at reduced intensity. On the basis of these experiments it was concluded that the continuous emission originated from a uranium oxide species.

Detailed examination of the emission in the wavelength region 5600 - 6100 $\overset{o}{A}$ using the Bausch and Lomb spectrograph revealed that the radiation was truly continuous. Unlike the spectra observed in the furnace, discrete line structure could not be observed at high resolution.

As has been indicated previously, UO_3 is expected to be the major uranium oxide species present in the flames. Therefore, it is not surprising to find that the flame spectra arc completely different from those observed in the furnace where U, UO and UO_2 are the major uranium containing species. At the present time, the processes leading to the observed continuum are unknown. However it is felt that the species involved may include UO_3 or more complex oxides and since these species may be important in disturbed environments, a more thorough study of the flame spectra is warranted.
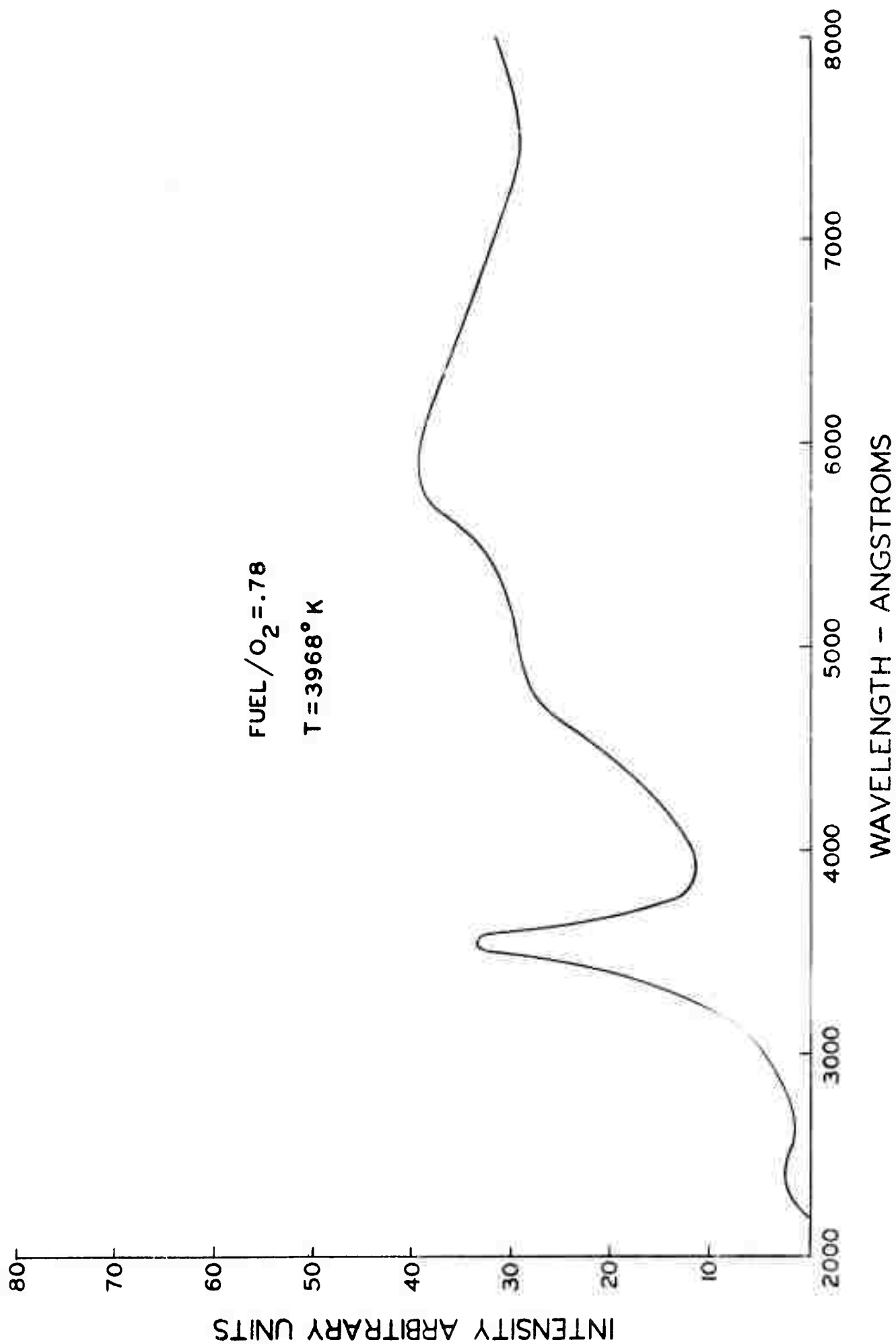
9

Figure 4.   Flame Spectra UF_6 Seeded C_2N_2/O_2 Flame

10

III. THORIUM OXIDE

1. Furnace Studies - Oscillator Strengths

ThO is characterized by extensive band spectra throughout the visible and near infrared regions. The analyses of several of these systems are fairly complete and the understanding of the ThO spectroscopy as compared to UO appears to be well in hand, (Ref. 6, 11). No absolute intensity data have been reported on any transitions for ThO. In light of the importance of ThO and the lack of intensity measurements for this molecule an experimental study was undertaken to obtain intensity information. The technique used was entirely analogous to that employed in the BaO study recently carried out in this laboratory (Ref. 12). Known partial pressures of ThO were generated by heating a mixture of liquid thorium and thoria to various temperatures. Total absorption measurements were made on several rotational lines in the $E\ ^1\Sigma \longrightarrow X\ ^1\Sigma$ system and the oscillator strengths for ThO (0,0) and (1,1) bands deduced. It should be noted that various electronic band systems have been observed in this study in <u>absorption</u> and it is anticipated that other electronic systems of ThO will be investigated in the near future.

In a fashion similar to that used in the uranium oxide studies, the carbon tube furnace was used to vaporize a mixture of liquid thorium-thoria so as to generate a known concentration of ThO. A mixture of equal amounts of thorium metal and thoria were loaded into a tantalum lined cylinderical carbon cell. The cell was $4\frac{1}{2}$ inches long and had tantalum lined carbon and end pieces with $1/4$ inch openings. The cell was degassed at approximately 1500°C under vacuum then pressurized to 1 atm. helium. Spectra were observed with the 2 meter B&L spectrograph and the Spex 1500 spectrometer.

It was found that the intensity of the bands slowly decreased with time at constant temperature. Apparently there is a decrease in the activity of thorium metal because of its slow solution into the thoria. Therefore, all quantitative measurements

were made as quickly as possible using a fresh mixture of thorium/thoria for each determination and with the B&L spectrograph rather than the scanning spectrometer.

A conventional optical arrangement was employed. This consisted of a 150-w Osram high pressure xenon light source whose beam was collimated and allowed to pass through the furnace. The beam was then focused to allow diaphragming out of unwanted light from the hot furnace walls and then refocused on to the slit of the spectrograph with a cylindrical quartz lens. A rotating step sector was used to calibrate each photographic plate so that relative intensity measurements could be made. 10μ slits were used with the 30,000 line/inch grating in the 1st order which gave a nominal plate dispersion of approximately $4\text{Å}/mm$. Estman Kodak type III-F plates were used to photograph the spectra. Optical densities were recorded directly with a Joyce-Loebl double beam microdensitometer.

Spectra of the $E\ ^1\Sigma \longrightarrow X\ ^1\Sigma$ system was recorded at temperatures between $2180^\circ C$ to $2345^\circ C$. A typical spectrum is shown in Figure 5. Indicated in this figure are the rotational lines selected for quantitative total absorption determinations. These were chosen on the basis of being least overlapped by other features. The total absorption i.e.

$$\int_0^\infty \frac{I_0 - I}{I_0}\ d\nu$$

(where I is the intensity at a frequency, ν, along a line profile,) were determined directly from the microdensitometer traces. These results at various temperatures are given in Table 1.

Assuming optically thin conditions, the total absorption, A, is given by (see Ref. 13)

$$A = \frac{\pi e^2}{m c}\ Nf\ell \tag{1}$$

$$= 2.654 \times 10^{-2}\ Nf\ell$$

where ℓ is the path length, e and m the charge and mass of the electron, N, the concentrations in molecules/cc of absorbers and f the oscillator strength of
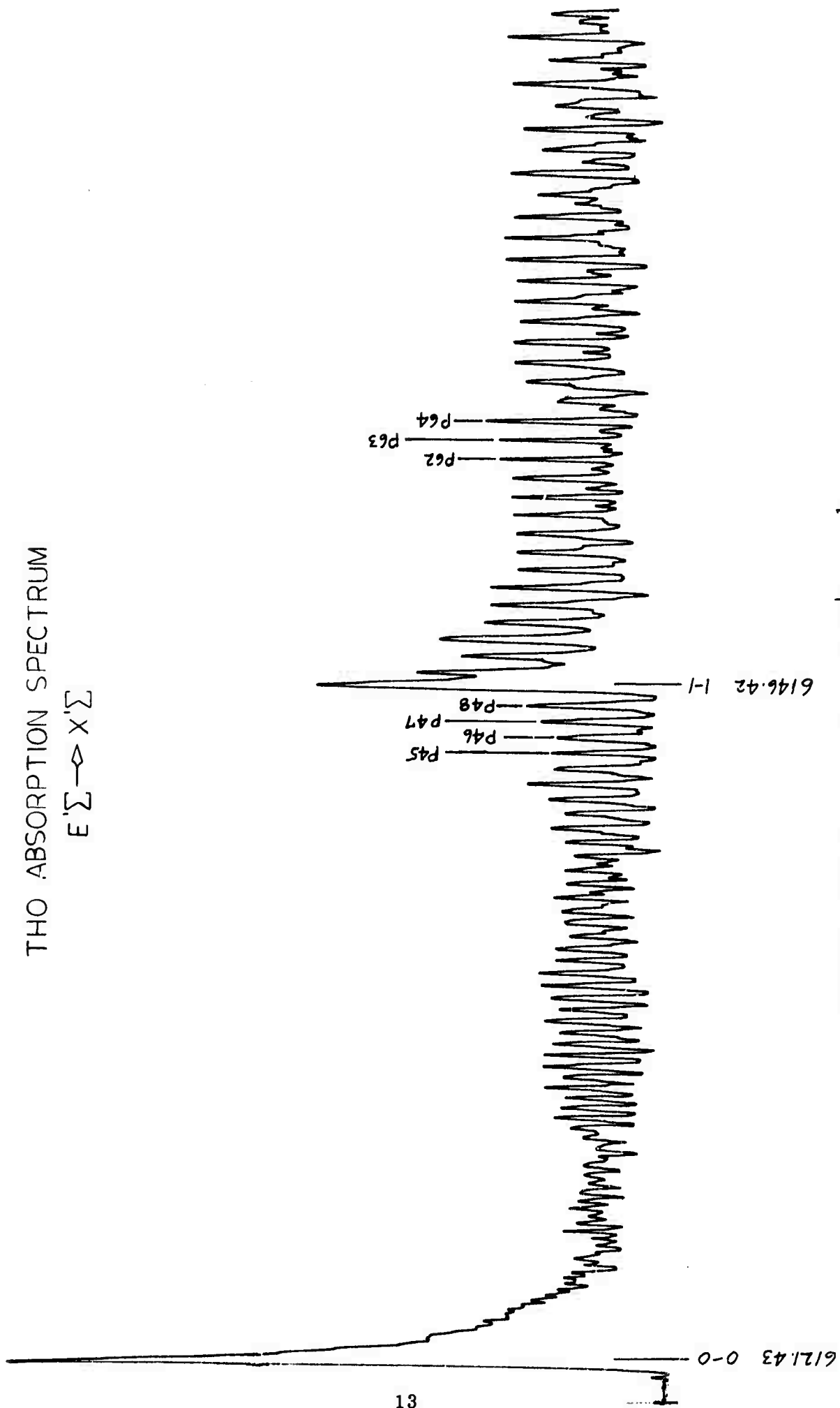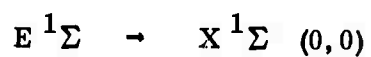
THO ABSORPTION SPECTRUM

E'Σ → X'Σ

P62 ——
P63 ——
P64 ——

P45 ——
P46 ——
P47 ——
P48 ——

6146.42 1-1 ——

6121.43 0-0 ——

Figure 5.   ThO Absorption Spectrum E $^1\Sigma$ - X $^1\Sigma$

13

TABLE I

TOTAL ABSORPTION MEASUREMENT FOR THO

$$E\ ^1\Sigma\ \rightarrow\ X\ ^1\Sigma\ (0,0)$$

TEMPERATURE °K	$A \times 10^{-9}$ (sec^{-1})						
	P(45)	P(46)	P(47)	P(48)	P(62)	P(63)	P(64)
2607	1.72	1.72	2.11	1.87	1.91	1.91	2.04
2520	1.01	1.06	1.05	1.24	1.10	1.10	1.16
2453	.93	.91	.80	.78	.90	--	.90
2503	1.22	1.09	1.11	1.28	1.34	1.44	1.39
2618	2.25	1.99	2.51	2.45	--	--	--
2562	1.35	1.33	1.34	1.51	1.75	1.53	1.54

the individual rotational line. The rotational line oscillator strengths are related to the so-called band oscillator strength by:

$$f_{line} = f_{band} \ S_j/2j + 1 \tag{2}$$

where S_j is the rotational line strength and j the rotational quantum number. The number of absorbers in any rotational level of the ground state is given by:

$$N = N_T (2j + 1) \ e^{-F_j/kT}/Q \tag{3}$$

where N_T is the total concentration of molecules, F_j is the rotational energy of the absorbing state and Q is the partition function. Substituting (3) and (2) into (1) gives:

$$A = 2.654 \times 10^{-2} \ f_{band} \ \ell \, N_T S_j \ e^{-F_j/kT}/Q \tag{4}$$

or

$$A = 2.654 \times 10^{-2} \ f_{band} \ \ell \, N_{jv} \tag{5}$$

where

$$N_{jv} = N_T \ S_j \ e^{-F_j/kT} \tag{6}$$

The quantity N_T was obtained from measured vapor pressures of ThO over mixtures of liquid thorium/thoria. Several sets of vapor pressure data for ThO are available in the literature. In the present case an average of the vapor pressure data reported by Darnell and McCollum (Ref. 14) and by Ackermann, Rauh and Thorn (Ref. 15) was used to derive values of N_T. Differences up to a factor of four between these two sets of data were encountered. Therefore, the derived N_T values could be in error by this amount. The partition function, Q, at the various temperatures was calculated from the free energy functions given by Brewer and Rosenblatt (Ref. 16) while the rotational energy levels for ground state ThO were taken from the observed spectrum given by Edvinsson et al (Ref. 15). S_j for a $^1\Sigma \longrightarrow ^1\Sigma$ transition is given by (Ref. 17):

$$S_j = J + 1 \quad \text{for R} \tag{7}$$
$$S_j = J \qquad \text{for P} \tag{8}$$

ℓ was taken to be 11.4 cm.

A plot of A vs the quantity $2.654 \times 10^{-2} \, \ell \, N_{jv}$ (equation 5) is shown in Figure 6. Although a great deal of scatter is evident a relatively good straight line can be placed through the points and the origin. The slope of this line yields directly the band oscillator strength $f_{0,0} = .08$.

The oscillator strength for the corresponding (1,1) band in the $E \, {}^1\Sigma \to X \, {}^1\Sigma$ system was estimated from the relative intensities of the (1,1) band at 6146.42 A to that of the (0,0) band at 6121.43 A and the ratio of populations in the first vibrational state to that of the ground state, i.e.

$$\frac{f_{1,1}}{f_{0,0}} = \frac{I_{1,1}}{I_{0,0}} \times \frac{N_0}{N_1} \tag{9}$$

N_0/N_1 was calculated using the spectroscopic constants of Edvinsson (Ref. 5). $f_{1,1}$ was found to be approximately equal to .06. The ratio $f_{0,0}/f_{1,1}$ compares favorably with the ratio of the corresponding Frank Condon factors, i.e. $g_{0,0}/g_{1,1}$, as obtained from a recent report by Wentink and Spindler (Ref. 6).

viz.
$$f_{0,0}/f_{1,1} = 1.33$$
$$g_{0,0}/g_{1,1} = 1.36$$

As mentioned earlier the largest source of error in these determinations is most likely due to the uncertaintly in the vapor pressures of ThO. Based on two sets of results this error could be as large as a factor of four. Until more reliable vapor pressure information becomes available, this uncertainty must be retained.

Figure 6. Curve of Growth for ThO $E^1\Sigma \to X^1\Sigma$
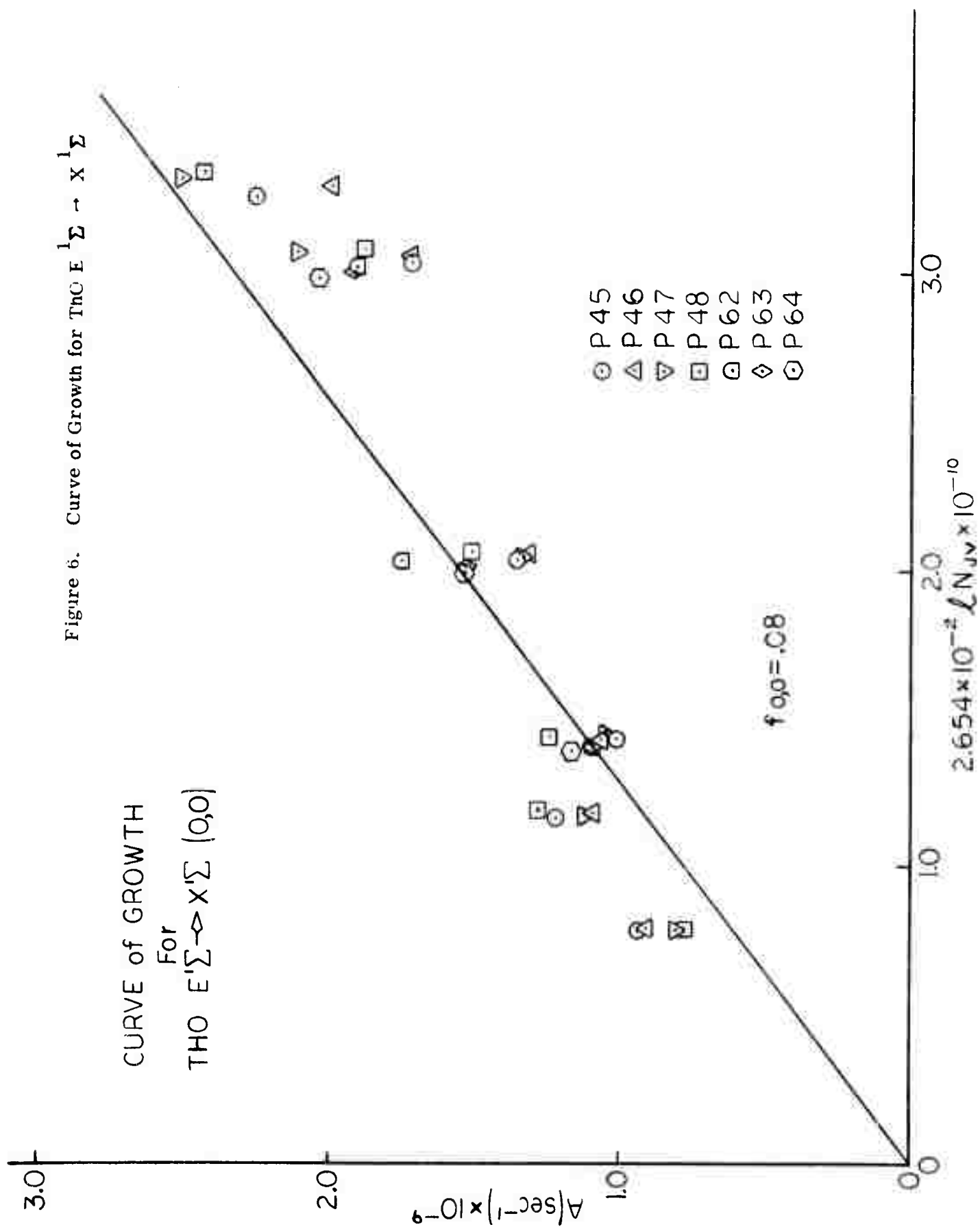
IV.   DISCUSSIONS AND RECOMMENDATIONS

It has been possible using the carbon tube furnace and strong reducing environments to obtain discrete spectra for either UO or UO_2. These spectra appear to be the best available to date.

It has been tentatively concluded, based on gross vibrational structure, that these spectra are most likely due to UO_2 rather than UO. The extreme complexity of the spectra is further evidence for the carrier being polyatomic rather than diatomic. The question as to the electronic spectrum of UO still remains unanswered. A technique similar to that used by Edvinsson et al (Ref. 15) for generating ThO spectra, viz. microwave discharge through a mixture of uranium and iodine in a neon carrier gas has been attempted with negative results. It is anticipated that during the next reporting period, excitation of UO spectra by microwave discharges through various UF_6 mixtures will be attempted. Work will continue on the interpretation of the furnace spectra.

It is felt that the results of the flame studies, initiated during the latter half of this reporting period, can be significant to the interests of Ivy Owl. Up until now only UO and UO_2 were being considered as important neutral species. Clearly when appreciable quantities of oxygen are also present, higher oxides such as UO_3 must also be considered. Further work on the seeded flames is being carried out.

It appears that reliable results on the oscillator strengths of various electronic transitions for ThO can be obtained from absorption measurements using the carbon tube furnace. Although the system presently studied is perhaps one of the simplest in the ThO spectra, extension to other transition should be quite feasible. It is anticipated that several other bands systems for ThO will be investigated.

18

ACKNOWLEDGEMENT

REFERENCES

1. A. Gatterer, J. Junkes, E. W. Saltpeter, and B. Rosen, "Molecular Spectra of Metallic Oxides", Specola Vaticana, Vatican City (1957).

2. R. Mavrodineanu and H. Boiteux, "Flame Spectroscopy", John Wiley & Sons, New York (1965).

3. T. Wentink, Jr., N. Pedersen, and G. Diebold, "Radiative Behavior of Metal Oxides in Laser Blowoff", DASA Report 2704, May 1971.

4. R. J. Ackermann, E. G. Rauh and M. S. Chandrasekharaiah, J. Phys. Chem., 73, 762 (1969).

5. G. DeMaria, R. P. Burns, J. Drowart, and M. G. Inghram, J. Chem. Phys., 32, 1373 (1960).

6. T. Wentink, Jr., and R. J. Spindler, Jr., "The Isoelectronic Series ScF through ThO, Part I". Preprint, Feb. 1972.

7. M. J. Linevsky, "Optical Energy Transfer Processes", Semiannual Report, Feb. 1968, ARPA #1009, ARPA Code #7E20, Project #7508-C, G.E. Co., King of Prussia, Penna.

8. D. W. Steinhaus and J. B. and M. Dringer, "Present Status of the Analysis of Arc Spectrum of Uranium (UI)", LA-3475, UC-34 Physics, TID-4500 (1966).

9. G. R. Harrison, et al, "M.I.T. Wavelength Tables", John Wiley & Sons, Inc., New York (1939).

10. S. Abramowitz, N. Acquista and K. R. Thompson, J. Phys. Chem., 75, 2282 (1971).

11. G. Edvinsson, L. E. Selin, and N. Aslund, Arkiv f. Fysik, 30, 283 (1965).

12. M. J. Linevsky, "Study of Optical Energy Transfer Processes", RADC-TR-70-212, Sept. 1970.

13. A.C.G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms", Cambridge University Press, 1961.

14. R. J. Ackermann, E. G. Rauh, and R. J. Thorn, J. Phys. Chem., 67, 762 (1963).

15.   A. J. Darnell and W. A. McCollum, NAA-SR-6498, Sept. 1961.

16.   L. Brewer and G. M. Rosenblatt, "Dissociation Energies and Free Energy
      Functions of Gaseous Monoxides",

17.   G. Herzberg, "Spectra of Diatomic Molecules", D. VanNostrand Co., Inc.
      1950.